SOLID STATE PHYSICS

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(iii) Reflections

A lattice is said to possess reflection symmetry if there exists a plane (or a line in two dimensions) in the lattice which divides it into two identical halves which are mirror images of each other. Such a plane (or line) is represented by *m*. The reflection symmetry of a notched wheel is illustrated in Fig. 1.8. Considering the combinations of reflections with allowed rotations, we note that each allowed rotation axis can be associated with two possibilities : one is rotation with reflection and the other rotation without reflection. Since there are five allowed rotation axes, the possible number of such combinations is 10. These are designated as

1, 1*m*, 2, 2*mm*, 3, 3*m*, 4, 4*mm*, 6, 6*mm*

where the numerals represent the type of rotation axis, the first *m* represents a plane (or line) parallel to the rotation axis and the second *m* refers to another plane (or line) perpendicular to the rotation axis. These ten groups of symmetry operations are shown in Fig. 1.9.
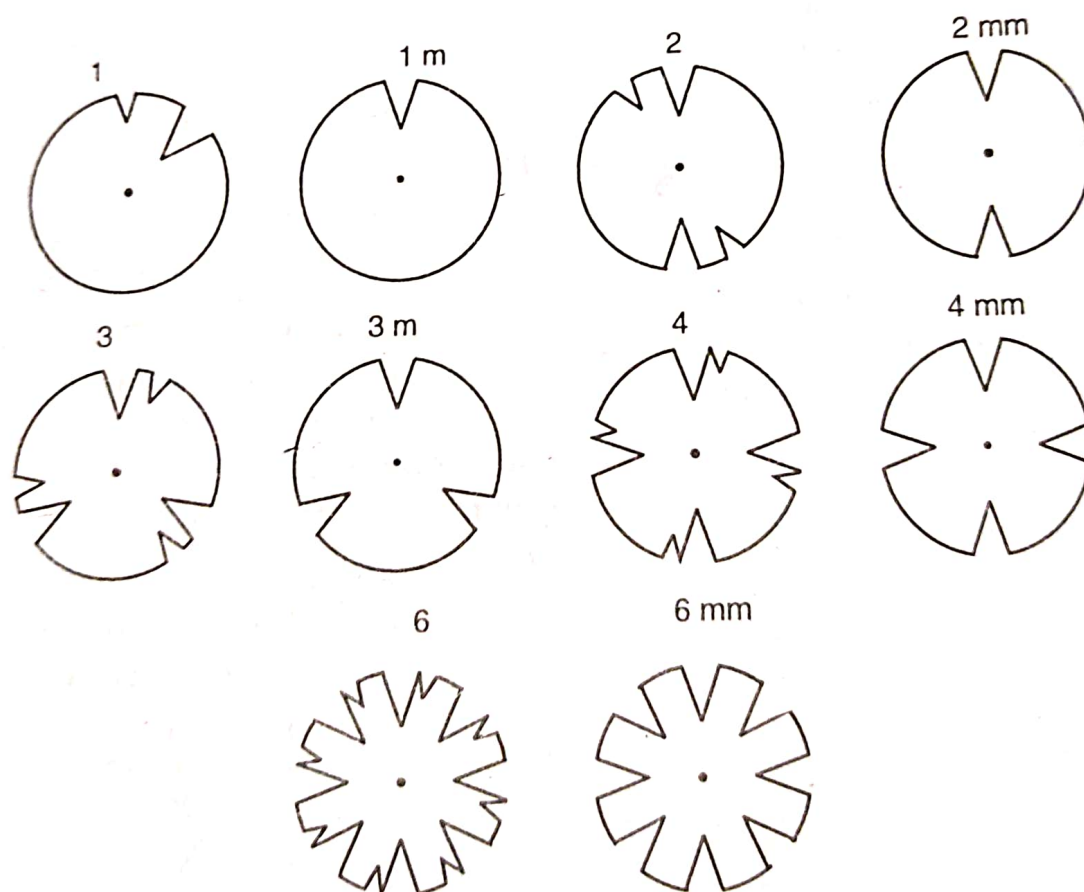
Fig. 1.9. *Ten two-dimensional point groups consisting of rotation and reflection symmetry operations illustrated using notched wheels.*

(iv) Inversions

Inversion is a point operation which is applicable to three-dimensional lattices only. This symmetry element implies that each point located at **r**

relative to a lattice point has an identical point located at −**r** relative to the same lattice point. In other words, it means that the lattice possesses a centre of inversion denoted by $\bar{1}$.

It may be noted that, apart from these symmetry operations, a three-dimensional lattice in particular may have additional symmetry operations formed by the combinations of the above-mentioned operations. One such example is *rotation-inversion operation*. These operations further increase the number of symmetry elements. These symmetry elements are further employed to determine the type of lattices possible in two and three-dimensional spaces.

1.6 POINT GROUPS AND SPACE GROUPS

We have seen that there are mainly four types of symmetry operations, i.e., translation, rotation, reflection and inversion. The last three operations are point operations and their combinations give certain symmetry elements which collectively determine the symmetry of space around a point. The group of such symmetry operations at a point is called a *point group.*

In two-dimensional space, rotation and reflection are the only point operations. As described earlier, their combinations yield 10 different point groups designated as 1, 1*m*, 2, 2*mm*, 3, 3*m*, 4, 4*mm*, 6, and 6*mm* which are shown in Fig. 1.9. In three-dimensional space, however, the situation is complicated due to the presence of additional point operations such as inversion. There are a total of 32 point groups in a three-dimensional lattice.

The crystals are classified on the basis of their symmetry which is compared with the symmetry of different point groups. Also, the lattices consistent with the point group operations are limited. Such lattices are known as *Bravais lattices*. These lattices may further be grouped into distinct crystal systems.

The point symmetry of crystal structure as a whole is determined by the point symmetry of the lattice as well as of the basis. Thus in order to determine the point symmetry of a crystal structure, it should be noted that

(*i*) a unit cell might show point symmetry at more than one locations inside it, and

(*ii*) the symmetry elements comprising combined point and translation operations might be existing at these locations.

The group of all the symmetry elements of a crystal structure is called *space group.* It determines the symmetry of a crystal structure as a whole. There are 17 and 230 distinct space groups possible in two and three dimensions respectively.

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1.7 TYPES OF LATTICES

As described earlier, the number of point groups in two and three dimensions are 10 and 32 respectively. These point groups form the basis for construction of different types of lattices. Only those lattices are permissible which are consistent with the point group operations. Such lattices are called *Bravais lattices*. It is beyond the scope of this book to describe the details of formation of various Bravais lattices from the possible point group operations. It can be stated that 10 and 32 point groups in two and three dimensions produce only 5 and 14 distinct Bravais lattices respectively. These Bravais lattices further become parts of 4 and 7 distinct *crystal systems* respectively and are separately described below.
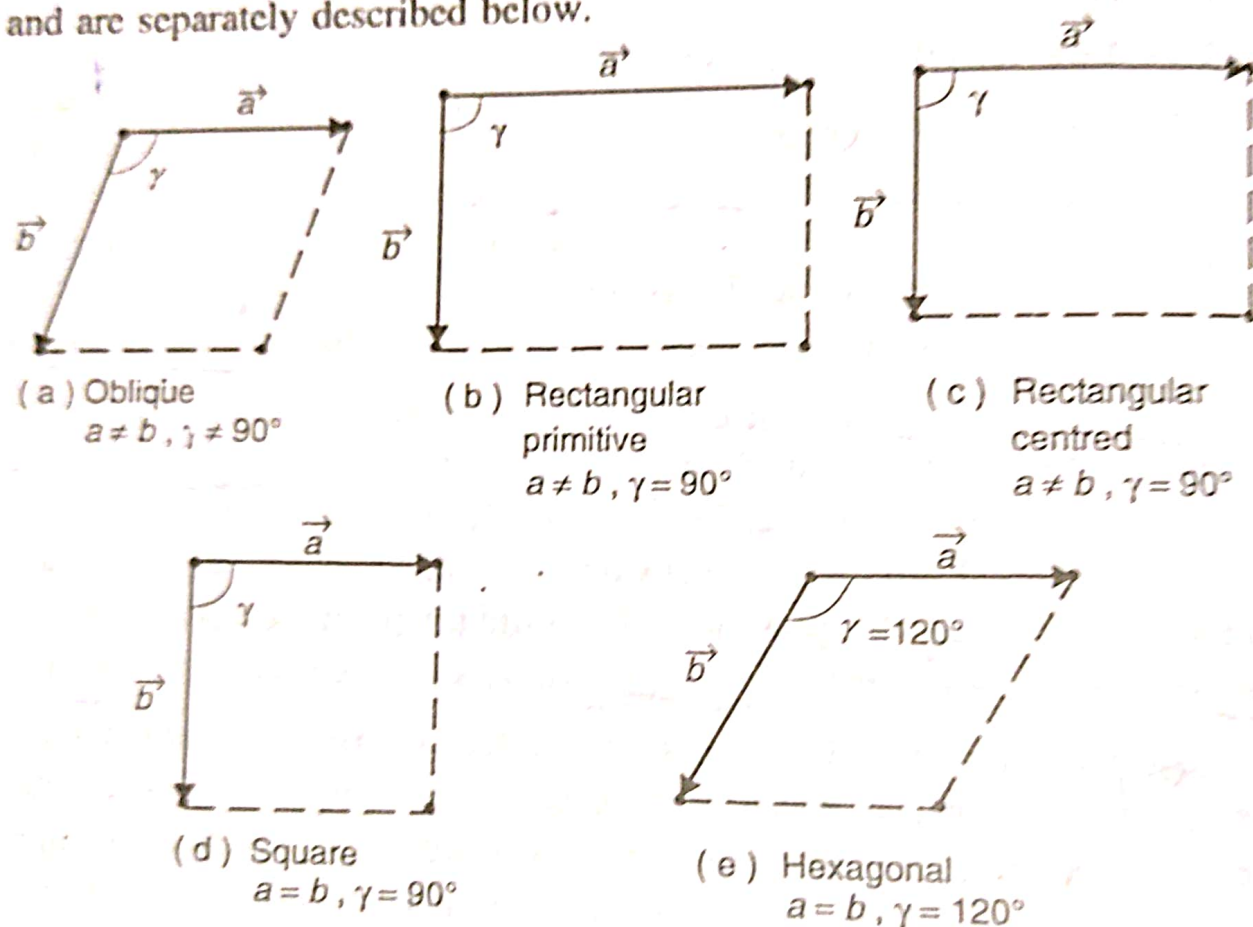

(a) Oblique
$a \neq b, \gamma \neq 90°$

(b) Rectangular primitive
$a \neq b, \gamma = 90°$

(c) Rectangular centred
$a \neq b, \gamma = 90°$

(d) Square
$a = b, \gamma = 90°$

(e) Hexagonal
$a = b, \gamma = 120°$

Fig. 1.10. *Bravais lattices in two dimensions.*

(i) Two-Dimensional Lattices

The four crystal systems of two-dimensional space are oblique, rectangular, square and hexagonal. The rectangular crystal system has two Bravais lattices, namely, rectangular primitive and rectangular centred. In all, there are five Bravais lattices which are listed in Table 1.1 along with the corresponding point groups. These lattices are shown in Fig. 1.10.

TABLE 1.1. Crystal systems and Bravais lattices in two dimensions

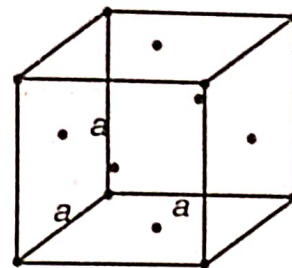| S. No.	Crystal system	Characteristic point group symmetry	Bravais lattice	Conventional unit cell	Unit cell characteristics
1	Oblique	1, 2	Oblique	Parallelogram	$a \neq b, \gamma \neq 90°$
2	Rectangular	$1m, 2mm$	1. Rectangular primitive	Rectangle	$a \neq b, \gamma = 90°$
			2. Rectangular centred		
3	Square	4, 4mm	Square	Square	$a = b, \gamma = 90°$
4	Hexagonal	3, 3m, 6, 6mm	Hexagonal	60° Rhombus	$a = b, \gamma = 120°$

(ii) Three-Dimensional Lattices

All the seven crystal systems of three-dimensional space and the corresponding Bravais lattices are listed in Table 1.2 in the decreasing order of symmetry. The crystallographic axes **a**, **b** and **c** drawn from one of the lattice points determine the size and shape of a unit cell. The angles α, β and γ represent the angles between the vectors **b** and **c**, **c** and **a**, and **a** and **b** respectively. The lengths a, b and c and angles α, β and γ are collectively known as *lattice parameters* or *lattice constants* of a unit cell. These Bravais lattices are also shown in Fig. 1.11 in the form of their conventional unit cells. The symbols P, F and I represent simple or primitive, face-centred, and body-centred cells respectively. A base or end-centred cell is that which has lattice points at corners and at one of the pairs of opposite faces. It is designated by the letter A, B or C. The designation A refers to the cell in which the faces defined by **b** and **c** axes contain the lattice points, and so on. The symbol R is specifically used for rhombohedral lattice.
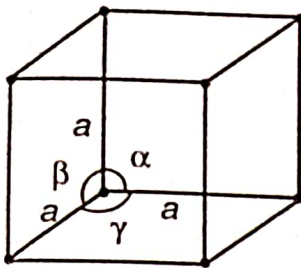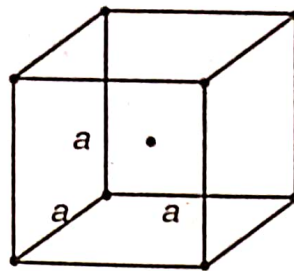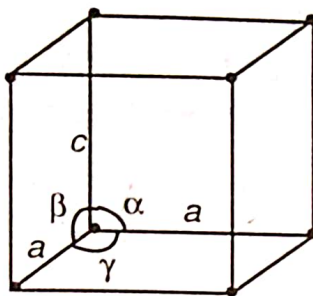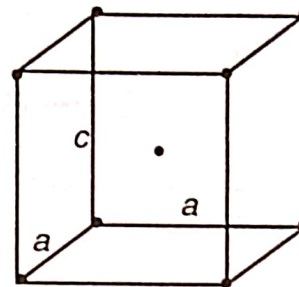
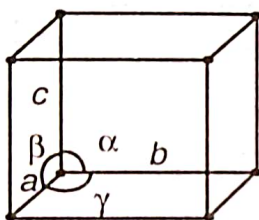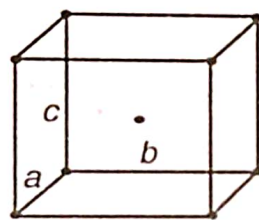Simple cubic (P)   Body – centred cubic (I)   Face – centred cubic (F)
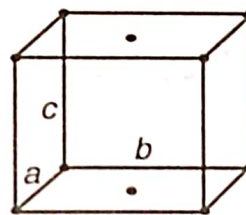
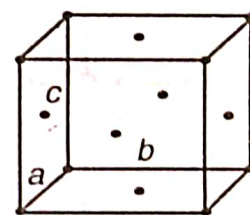Simple tetragonal (P)   Body – centred tetragonal (I)
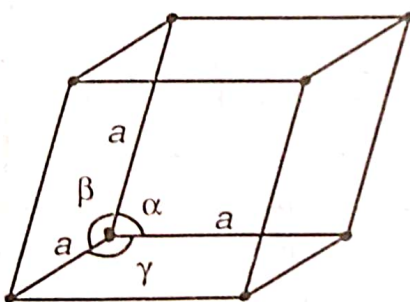
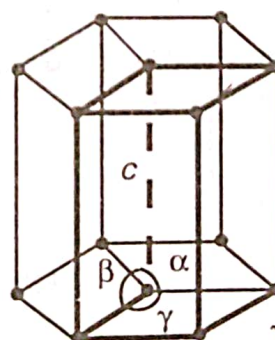Simple orthorhombic (P)   Body – centred orthorhombic (I)   End – centred ortharhombic (C)   Face – centred orthorhombic (F)
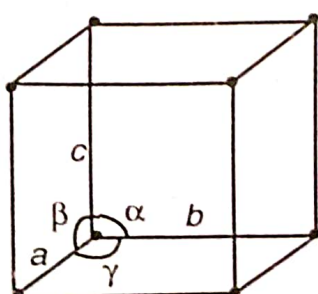
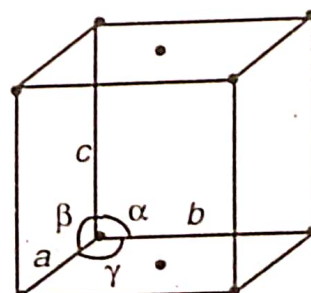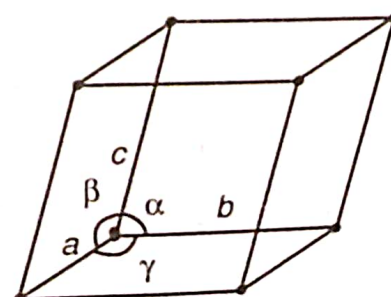Simple rhombohedral (R)   Simple hexagonal (P) $\gamma = 120°$

Simple monoclinic (P)   End – centred monoclinic (P)   Simple triclinic (P)

Fig.1.11. *The Bravais lattices in three dimensions*

TABLE 1.2. Crystal systems and Bravais lattices in three dimensions

S. No.	Crystal system	Lattice parameters	Bravais lattice	Common abbreviation	Lattice symbol	Examples
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Simple Body-centred Face-centred	sc bcc fcc	P I F	Cu, Ag, Fe, Na, NaCl, CsCl
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple Body-centred	st bct	P I	β-Sn, TiO_2
3	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple Body-centred End-centred Face-centred	so bco eco fco	P I C F	Ga, Fe_3C (cementite)
4	Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	Simple	–	P (or R)	As, Sb, Bi
5	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°,$ $\gamma = 120°$	Simple	–	P	Mg, Zn, Cd, NiAs
6	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	Simple End-centred	– –	P C	$CaSO_4 \cdot 2H_2O$ (gypsum)
7	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	Simple	–	P	$K_2Cr_2O_7$

The hexagonal crystal system has only one Bravais lattice and its unit cell may be either of cubical or of hexagonal type. The cubical type cell (outlined by thick lines) has lattice points only at the corners. The hexagonal cell has lattice points at the corners as well as at the centres of the two hexagonal faces. One hexagonal cell is formed by joining together three cubical type cells.

A lattice point lying at the corner of a cell is shared by eight such cells and the one lying at the face centre position is shared by two cells. Therefore, the contribution of a lattice point lying at the corner towards a particular cell is 1/8 and that of a point lying at the face centre is ½. The following equation is used to calculate the effective number of lattice points, N, belonging to a particular cell :
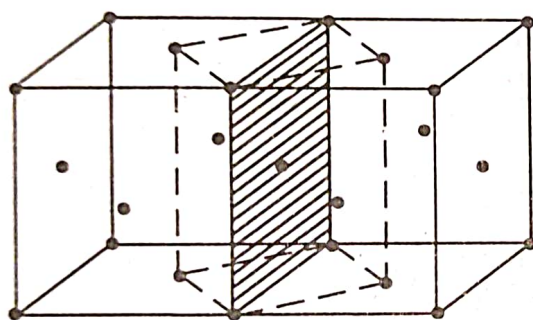
$$N = N_i + N_f/2 + N_c/8 \qquad\qquad (1.5)$$

where N_i represents the number of lattice points present completely inside the cell, and N_f and N_c represent the lattice points occupying face centre and corner positions of the cell respectively. Using this relation, the effective number of lattice points in a simple cubic, body-centred cubic and face-centred cubic lattices comes out to be 1, 2 and 4 respectively.

Fig. 1.12. *Two face-centred tetragonal lattices placed side by side result in an end-centred tetragonal lattice shown by dotted lines.*

The list of Bravais lattices given in Table 1.2 appears to be incomplete. The orthorhombic system contains four Bravais lattices whereas the cubic and tetragonal systems contain only three and two lattices respectively. It can be shown that the lattices which are absent in certain crystal systems do not result in new types of arrangements and so need not be considered separately. Figure 1.12 shows two face-centred tetragonal lattices placed side by side. This arrangement of points, shown by dotted lines, produces body-centred tetragonal lattice which already exists in the Bravais list.

1.8 LATTICE DIRECTIONS AND PLANES

The direction of a line in a lattice is defined by assigning certain indices to this line. If the line passes through the origin, its indices are determined by taking a point on this line and finding out the projections of the vector drawn from the origin to that point on the crystallographic axes. Let these projections be u, v and w. Apparently, u, v and w also represent the coordinates of that point. These coordinates are then simplified to get a set of the smallest possible integers which when enclosed in square brackets represent the indices of the line. As an example, to determine the indices of the direction OQ in a cubic crystal (Fig. 1.13), we may take either a point P (½, ½, ½) or Q (1, 1, 1) on this line; either of these points yields the indices of the direction OQ as [111]. The same are the indices of any other direction parallel to OQ because by shifting the origin to an appropriate position, the new direction can be made to pass through the points O, P and Q. The origin is shifted in such a way that the orientation of the axes remains unchanged. If a direction is perpendicular to a certain axis, its index corresponding to that axis is zero as it does not form any projection on the axis. A direction having projections on the negative sides of the axes possess negative indices which are written by putting bars over the indices.

Consider the direction AB as shown in Fig. 1.14. The indices of this
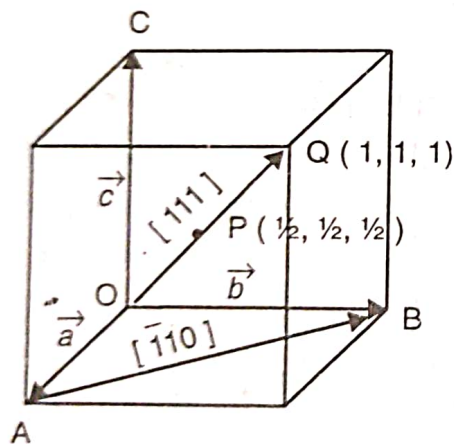
Fig. 1.13. *Determination of indices of a direction.*

Fig. 1.14. *Indices of some directions in a cubic lattice.*

direction can be obtained by shifting the origin to the point A'. The projections of AB on the axes then become –1, 1, and 0 and hence the indices of the line AB are [$\bar{1}$10]. The indices of a few more directions are illustrated in Fig. 1.14. The cube edges are represented by the indices of the type [100], [010], [$\bar{1}$00], etc. These constitute a family of cube edges designated as <100> which includes all the directions of this type. Similarly, a

family of face diagonals is represented by <110> and that of body diagonals by <111>. The number of members in the families of cube edges, face diagonals and body diagonals is 6, 12 and 8 respectively.

The angle θ between the two crystallographic directions [hkl] and [$h'k'l'$] is given by

$$\cos\theta = \frac{hh' + kk' + ll'}{(h^2 + k^2 + l^2)^{1/2} (h'^2 + k'^2 + l'^2)^{1/2}} \qquad (1.6)$$

The scheme to represent the orientation of planes in a lattice was first introduced by Miller, a British crystallographer. The indices of planes are, therefore, known as the *Miller indices*. The steps involved to determine the Miller indices of a plane are as follows :

    (i)   Find the intercepts of the plane on the crystallographic axes.

    (ii)   Take reciprocals of these intercepts.

    (iii)   Simplify to remove fractions, if any, and enclose the numbers obtained into parentheses.

In step (i), the intercepts are taken in terms of the lengths of fundamental vectors choosing one of the lattice points as the origin. If a plane is parallel to a certain axis, its intercept with that axis is taken as infinity. In step (ii) the reciprocals are taken in order to avoid the occurrence of infinity in the Miller indices.

As an example, consider a plane ABC (Fig. 1.15) having intercepts 1, 2 and 1 with the crystallographic axes a, b and c respectively of a cubic lattice. The Miller indices of this plane are determined as follows :

    (i)   Intercepts   : 1, 2, 1

    (ii)   Reciprocals   : 1, ½, 1

    (iii)   Simplification : 2, 1, 2

Hence the Miller indices of the plane ABC are (212) ; the numbers within the parentheses are written without commas. The Miller indices of a plane, in general, are written as (*hkl*).

It may be noted that another plane DEF which is parallel to the plane ABC and lies completely inside the lattice, has intercepts 1/2, 1 and 1/2 with the
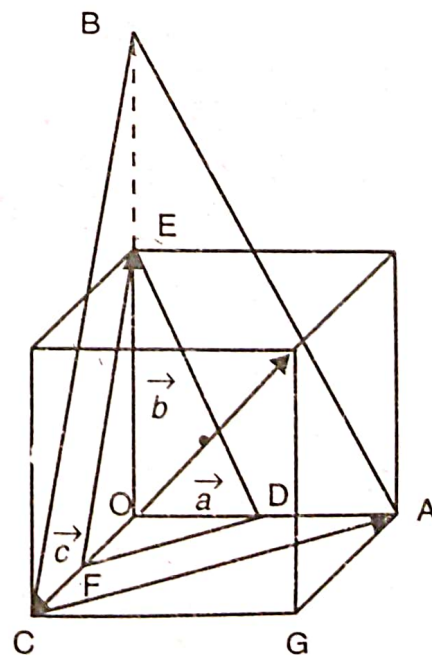

Fig. 1.15. *Miller indices of parallel planes and the planes passing through the origin.*

axes and hence carries the same Miller indices as the plane ABC. Thus we conclude that the parallel planes have the same Miller indices. The plane DEF is rather more convenient to deal with as it lies completely inside the lattice.

If a plane intercepts an axis on the negative side, a bar is put above the corresponding number of the Miller indices. The intercepts of a plane passing through the origin cannot be determined as such. In such a case, we take another plane parallel to this plane and determine its Miller indices. The same are the indices of the given plane. Alternatively, we shift the origin from the plane to some other suitable lattice point without changing the orientation of the axes and then find the Miller indices. For example, the indices of the plane OCGA in Fig. 1.15 become $(0\bar{1}0)$ if the origin is shifted to the point E. The importance of orientation of the axes can be realized with reference to Fig. 1.12. The indices of the shaded plane are of the type (100) when referred to the axes of the face-centred tetragonal cell, whereas these become of the type (110) when referred to the axes of the simple tetragonal cell indicated by dotted lines.

A family of planes of a particular type is represented by enclosing the Miller indices of any one of the planes of that family into braces. Thus {100} represents a family of planes which has the planes (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$ and $(00\bar{1})$ as its members. These six planes represent the faces of the cube. Similarly, the families of diagonal planes and close-packed planes are represented by {110} and {111}, and contain 6 and 8 members respectively. Some of these planes are illustrated in Fig. 1.16.

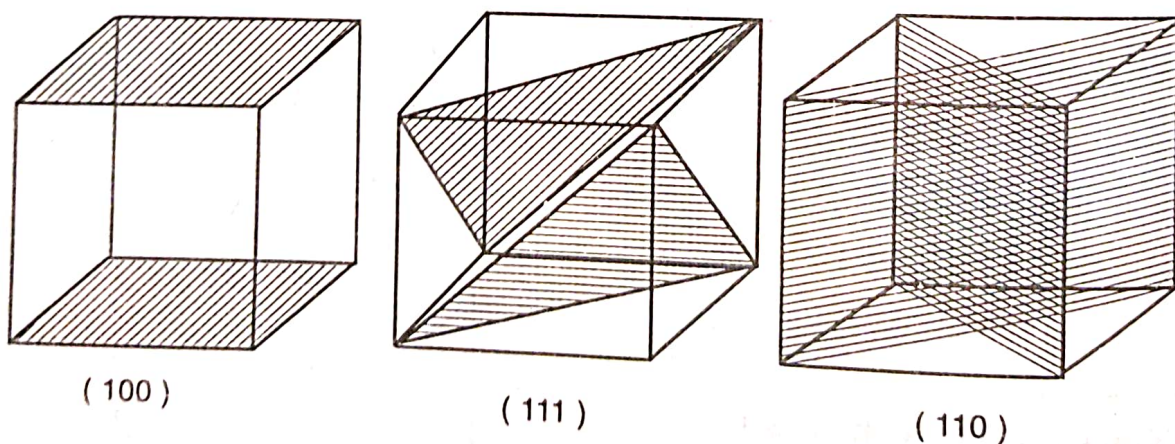(100)   (111)   (110)

Fig. 1.16. *Two parallel planes belonging to each one of the families {100}, {111} and {110} in a cubic lattice.*

1.9 INTERPLANAR SPACING

Consider a set of parallel planes with indices (hkl). Take origin on a

lattice point of one such plane and draw crystallographic axes **a**, **b** and **c**. Now consider another similar plane adjacent to this plane. Since the second plane also has the Miller indices (*hkl*), the lengths of the intercepts on **a**, **b** and **c** are *a/h*, *b/k* and *c/l* respectively. If we draw a normal from the origin to the second plane, the length of the normal represents the interplanar distance *d*. From Fig. 1.17, it follows that

$$d = OP = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma \qquad (1.7)$$
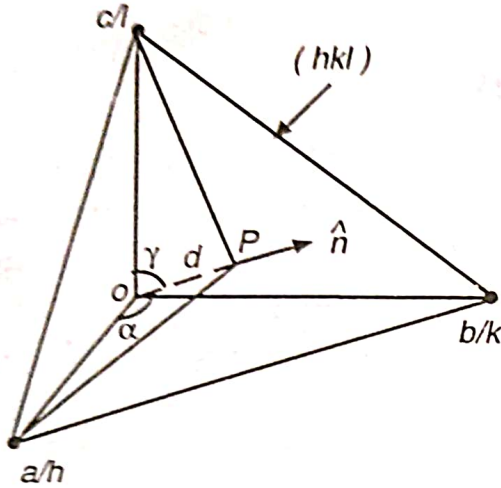
where α, β and γ represent the angles between the normal and the axes **a**, **b** and **c** respectively and cos α, cos β and cosγ represent the direction cosines of the normal to the plane (*hkl*). The Eq. (1.7) indicates that the direction cosines of the normal are proportional to *h/a*, *k/b* and *l/c*.

If $\hat{n}$ be the unit vector of the normal to the plane, then $a \cos\alpha$, $b \cos\beta$ and $c \cos\gamma$ may be written as $\hat{n}.\mathbf{a}$, $\hat{n}.\mathbf{b}$ and $\hat{n}.\mathbf{c}$ respectively and Eqs. (1.7) become

Fig. 1.17. *An (hkl) plane at a distance d from another similar parallel plane passing through the origin.*

$$d = \hat{n}.\mathbf{a}/h = \hat{n}.\mathbf{b}/k = \hat{n}.\mathbf{c}/l \qquad (1.8)$$

Thus the value of *d* can be determined if $\hat{n}$ is known. In an orthogonal lattice, where **a**, **b** and **c** point along *x*, *y* and *z* directions respectively, the equation of the plane (*hkl*) with intercepts *a/h*, *b/k* and *c/l* on the axes is

$$f(x, y, z) = hx/a + ky/b + lz/c = 1$$

For a surface $f(x, y, z)$ = constant, ∇f represents the vector normal to it.

$$\therefore \qquad \hat{n} = \frac{\nabla f}{|\nabla f|} = \frac{(h/a)\hat{i} + (k/b)\hat{j} + (l/c)\hat{k}}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}}$$

Hence from Eqs. (1.8), we obtain

$$\mathbf{d} = \frac{\hat{n}.\mathbf{a}}{h} = \frac{\left[(h/a)\hat{i} + (k/b)\hat{j} + (l/c)\hat{k}\right].(a/h)\hat{i}}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}}$$

or

$$d = \frac{1}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}} \qquad (1.9)$$

This equation is valid for orthogonal lattices only. For non-orthogonal lattices, such an expression may not be obtained easily; one may need to find $\hat{n}$ by some other method and then use Eq. (1.8) to determine d. For a cubic lattice, a, b and c are equal and we get

$$d = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}} \qquad (1.10)$$

It may also be noted that for a cubic lattice, the direction [hkl] is perpendicular to the plane (hkl).

1.10 SIMPLE CRYSTAL STRUCTURES

We shall now describe some of the basic crystal structures which are either monoatomic or contain simple basis. These include *close-packed structures* like hexagonal close-packed or face-centred cubic structures and *loose-packed structures* like body-centred cubic or simple cubic structures. Besides these, the structures of diamond, zinc blende and sodium chloride are also described.

1.10.1. Close-Packed Structures

Close-packed structures are mostly found in monoatomic crystals having non-directional bonding, such as metallic bonding. In these structures, the coordination number of each atom is 12, i.e., each atom is surrounded by twelve similar and equal sized neighbours. Out of these twelve neighbours, six lie in one plane, three in an adjacent parallel plane above this plane and three in a similar plane below it. There are two types of close-packed structures :

   (i)   Hexagonal close-packed (hcp) structure

   (ii) Face-centred cubic (fcc) structure

These structures are described as follows :
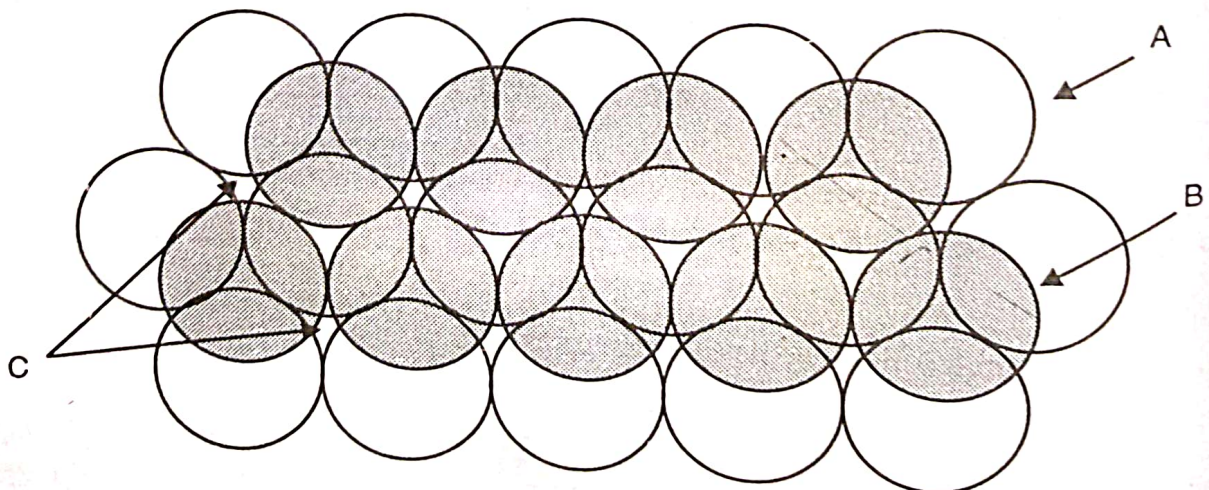

Fig. 1.18. *Layered arrangement of close-packed structures.*
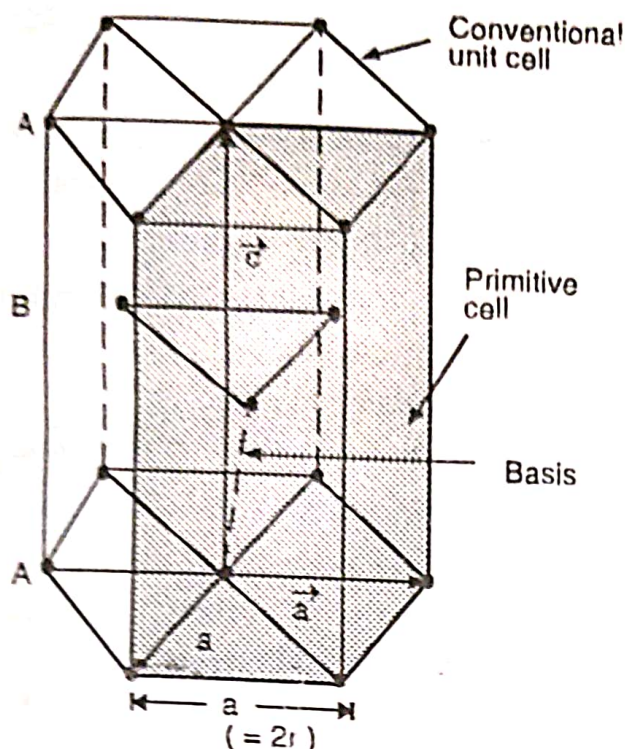
(i) Hexagonal Close-Packed Structure

Consider a layer of similar atoms with each atom surrounded by six atoms in one plane as shown in Fig. 1.18. Another similar layer B can be placed on top of layer A such that the atoms of layer B occupy the alternate valleys formed by the atoms of layer A. If a third similar layer is placed on top of the B-layer in such a way that the atoms of B-layer exactly overlap the atoms of A-layer and this type of stacking is repeated successively, the following layered arrangement is obtained :

....ABABAB....

Fig. 1.19. *Conventional and primitive cells of hexagonal close-packed structure.*

This type of stacking is called *hcp stacking* and the structure is known as *hexagonal close-packed structure.* The name corresponds to the shape of the conventional unit cell which is hexagonal and is shown in Fig. 1.19. There are twelve atoms located at the corners, two at the centres of the basal planes, and three completely inside the hexagon forming a part of the B-layer. The effective number of atoms in a unit cell is

$$12(1/6) + 2(1/2) + 3 = 6$$

The interatomic distance for the atoms within a layer is a. The distance between the two adjacent layers is $c/2$, c being the height of the unit cell. For an ideal *hcp* structure, $c = 1.633a$.

It may be noted that although the structure is *hcp*, the space lattice is simple hexagonal with basis consisting of two atoms placed in such a way that if one atom lies at the origin, the other atom lies at the point $(2/3, 1/3, 1/2)$. The shaded portion in Fig. 1.19 represents the primitive cell of this structure. It contains 2 atoms instead of one which is due to the presence of the basis. Also, the volume of the primitive cell is exactly one-third of the volume of the hexagonal cell.

The *packing fraction, f,* is defined as the ratio of the volume occupied by the atoms present in a unit cell to the total volume of the unit cell. It is also referred to as the *packing factor* or *packing efficiency* of the unit cell. From the primitive cell, we find
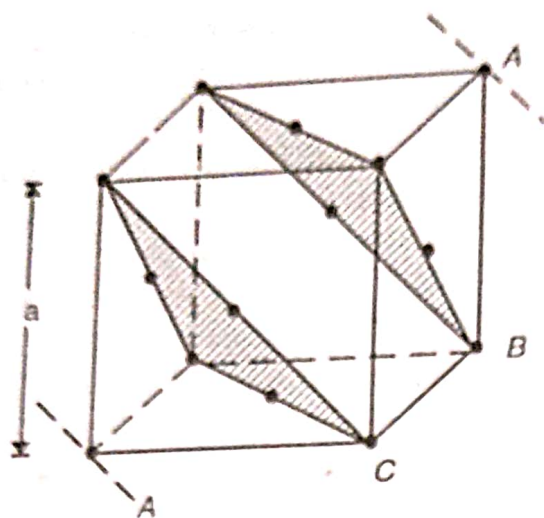
$$f = \frac{2(4/3)\pi r^3}{a(a \sin 60°)c}$$

where r is the atomic radius. Using $c = 1.633a$ and $a = 2r$, we get

$$f = 0.74$$

Thus, in an ideal *hcp* structure, 74% of the total volume is occupied by atoms. Metals like Mg, Zn, Cd, Ti, etc. exhibit this type of structure.

(ii) Face-Centred Cubic Structure

In this structure, the stacking of first two layers A and B is similar to that of hcp structure. The difference arises in the third layer which, in the present case, does not overlap the first layer. The atoms of the third layer occupy the positions of those valleys of the A-layer which are not occupied by the B-layer atoms. The third layer is designated by the letter C. The fourth layer exactly overlaps the first layer and the sequence is repeated. Thus *fcc* structure is represented by the following stacking sequence :

Fig. 1.20. *Conventional unit cell of fcc structure along with the stacking sequence .... ABCABC ....*

.... ABCABCABC ....

The conventional unit cell is *face-centred cubic* and is shown in Fig. 1.20. It is a non-primitive cell having effective number of atoms equal to 8 (1/8) + 6 (1/2) or 4. The atoms touch one another along the face diagonals. The length of the cube edge, a, and the atomic radius, r, are related to each other as

$$4r = \sqrt{2}\,a$$

The packing fraction, f, is given by

$$f = \frac{4(4/3)\pi r^3}{a^3} = 0.74$$

Thus the packing fraction of *fcc* structure is exactly the same as that of hcp structure which is expected because of the close-packed nature of both the structures. Also, the coordination number of each atom is 12. Examples of materials having this type of structure are Cu, Ag, Au, Al, etc.

1.10.2. Loose-Packed Structures

A loose-packed structure is that in which the coordination number of an atom is less than 12 or the packing fraction is less than 0.74. Among the various possible loose-packed structures, the most common and the simplest are the *body-centred cubic (bcc)* and the *simple cubic (sc)* structures. These structures are described as follows :

(i) Body-Centred Cubic Structure (bcc)

The conventional unit cell of *bcc* structure is non-primitive and is shown in Fig. 1.21. It has cubical shape with atoms located at the corners and the body centre. Thus the effective number of atoms per unit cell is $8(1/8) + 1 = 2$. The coordination number of each atom is 8. The atoms touch one another along the body diagonal. Thus a is related to r as

$$4r = \sqrt{3}\, a.$$

The packing fraction is given by

$$f = \frac{2(4/3)\pi r^3}{a^3} = 0.68$$

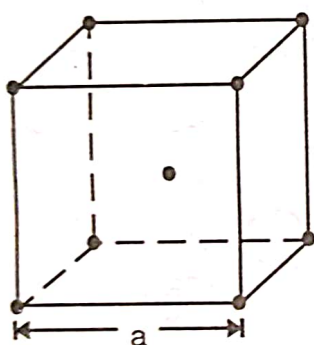The examples of materials exhibiting *bcc* structure are Na, K, Mo, W, etc.

Fig. 1.21. *Conventional unit cell of bcc structure.*
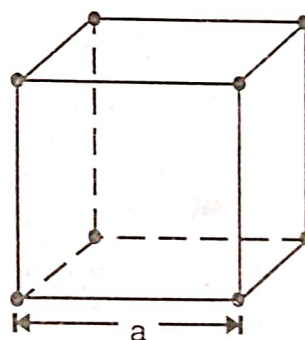
Fig. 1.22. *Unit cell of sc structure.*

(ii) Simple Cubic Structure (sc)

The conventional unit cell of *sc* structure is the same as its primitive cell and is shown in Fig. 1.22. The atoms are located at the corners only and touch one another along the cube edges. Thus in *sc* structures, we have

$$a = 2r$$

The coordination number of each atom is 6. The packing fraction is given by

$$f = \frac{1(4/3)\pi r^3}{a^3} = 0.52$$

Only polonium exhibits this type of structure at room temperature.

1.11　STRUCTURE OF DIAMOND

Diamond exhibits both cubic and hexagonal type structures. The diamond cubic (*dc*) structure is more common and is described here. The space lattice of the diamond cubic structure is *fcc* with basis consisting of two carbon atoms, one located at the lattice point and the other at a distance of one quarter of the body diagonal from the lattice point along the body diagonal. The unit cell of the *dc* structure is shown in Fig. 1.23. The carbon atoms placed along the body diagonals, in fact, occupy the alternate tetrahedral void positions in the *fcc* arrangement of carbon atoms. This opens up the otherwise close-packed *fcc* arrangement which decreases the packing efficiency considerably. The packing efficiency of the *dc* structure is only 34% as compared to 74% for the *fcc* structure. The coordination number of each carbon atom is 4 and the nearest neighbour distance is equal to $\sqrt{3}a/4$ where a is the lattice parameter.

The *dc* structure may also be viewed as an interpenetration of two *fcc* sublattices with their origins at (0, 0, 0) and (1/4, 1/4, 1/4). A plan view of the positions of all the carbon atoms in the unit cell is shown in Fig. 1.24. The fractional heights of the carbon atoms relative to the base of the unit cell are given in the circles drawn at the atomic positions. Two numbers in the same circle indicate two carbon atoms at the same position located one above the other. Other materials exhibiting this type of structure are Si, Ge, SiC, GaAs, gray tin, etc.
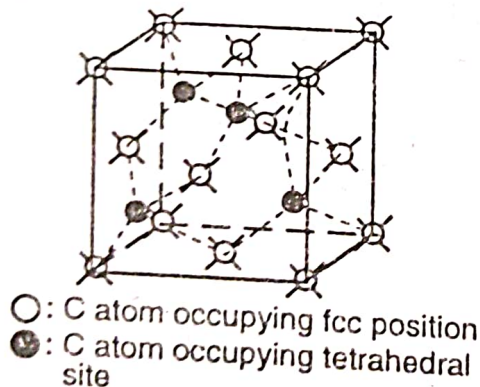

O: C atom occupying fcc position
●: C atom occupying tetrahedral
　　site

Fig. 1.23. *The unit cell of dc structure. The lattice is fcc with carbon atoms located at fcc positions and at alternate tetrahedral sites.*
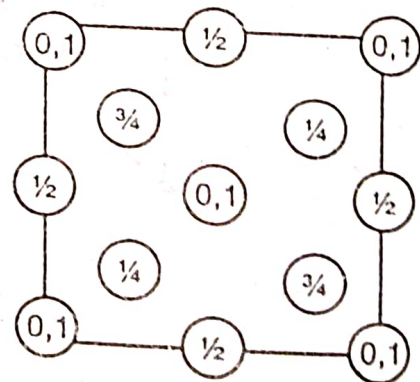
Fig. 1.24. *Plan view of atomic positions in dc unit cell. Numbers in the circles indicate fractional heights of the carbon atoms.*

1.12　ZINC BLENDE (ZnS) STRUCTURE

The zinc blende structure is similar to the *dc* structure except that the two *fcc* lattices in it are occupied by different elements. The structure is similar to the one shown in Fig. 1.23 where the dark circles now represent one type of atoms, say Zn, and the light circles represent the other type of atoms, i.e., S.

1.13 SODIUM CHLORIDE (NaCl) STRUCTURE

The unit cell of NaCl structure is shown in Fig. 1.25. In NaCl structure, the radii of Na⁺ and Cl⁻ ions are such that each Na⁺ ion is octahedrally coordinated to six Cl⁻ ions. The unit cell is *fcc* with four Cl⁻ ions occupying all the four *fcc* positions and the four Na⁺ ions occupying all the four octahedral voids. The *fcc* positions and the octahedral void positions are, however, interchangeable. The NaCl structure can, therefore, be viewed
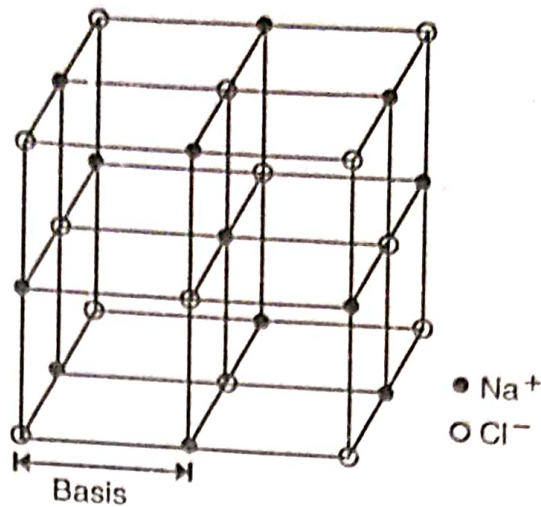

Fig. 1.25. *Unit cell of sodium chloride structure.*

as two interpenetrating *fcc* sublattices, one belonging to Na⁺ ions with its origin at the point (0, 0, 0) and the other belonging to Cl⁻ ions with its origin at the point ($a/2$, 0, 0). In the terminology of lattice and basis, the structure can be interpreted as an *fcc* lattice with basis consisting of two ions, one of Na⁺ and the other of Cl⁻. One of these ions occupies one of the *fcc* positions and the other ion occupies the corresponding octahedral void position. A unit cell of NaCl comprises four molecules. The position of various ions in the unit cell are as follows :

Na⁺ : 0, 0, 0; 1/2,1/2,0; 1/2,0,1/2; 0,1/2,1/2

Cl⁻ : 1/2,1/2,1/2; 0,0,1/2; 0,1/2,0; 1/2,0,0

SOLVED EXAMPLES

Example 1.1 Determine the relationships between the lattice parameter a and the atomic radius r for monoatomic *sc*, *bcc* and *fcc* structures.

Solution. In *sc* structure (Fig. 1.26), the atoms touch one another along the cube edges.

∴
$$a = 2r$$

In *bcc* structure, the atoms touch along the body diagonals.

∴
$$\sqrt{3}a = 4r$$

or
$$a = 4r/\sqrt{3}$$

In *fcc* structure, the atoms touch along the face diagonals.
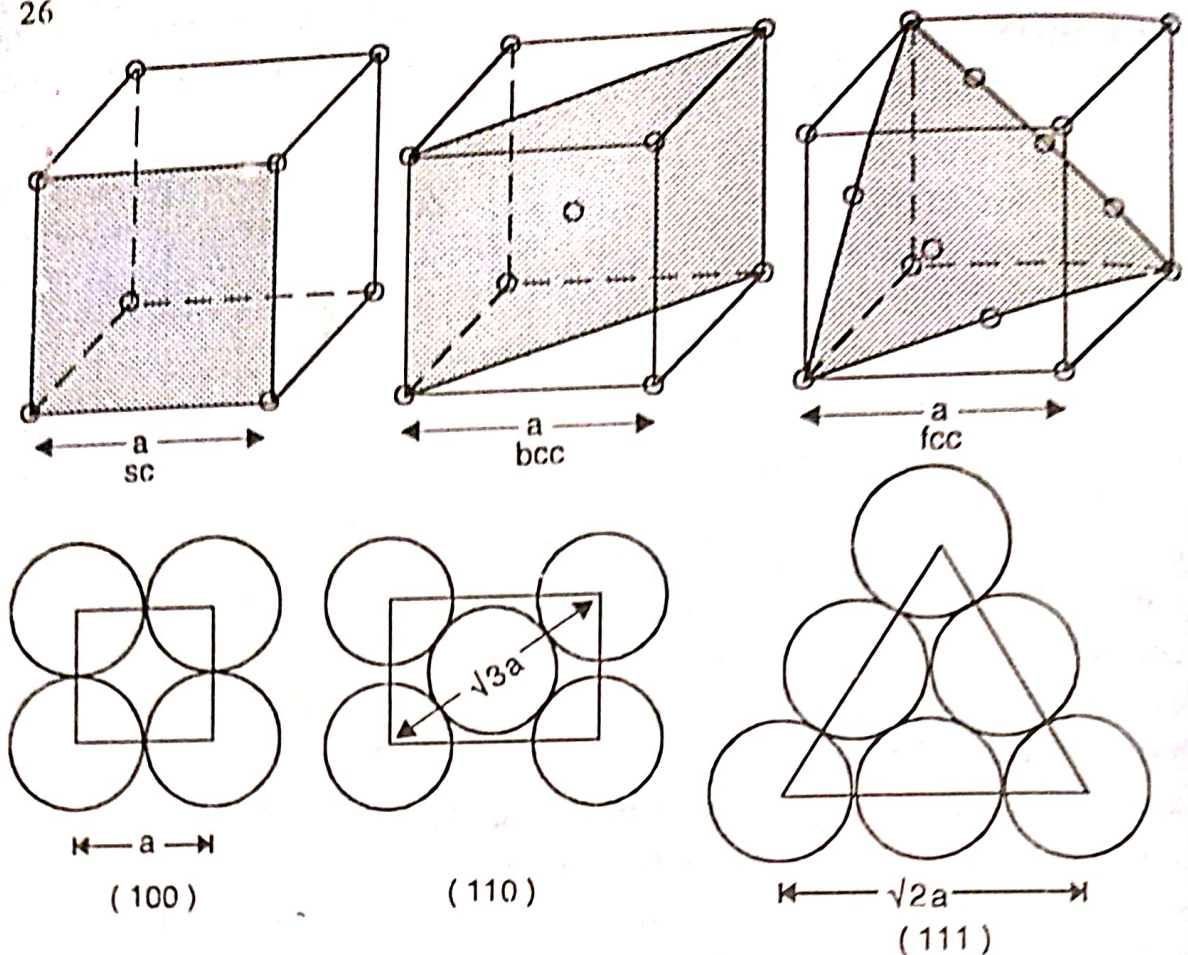
∴
$$\sqrt{2}a = 4r$$

or
$$a = 2\sqrt{2}r$$

Fig. 1.26. *Monoatomic sc, bcc and fcc structures along with their (100), (110)
and (111) type planes respectively.*

Example 1.2. Draw (101) and (111) planes in a cubic unit cell. Determine
the Miller indices of the directions which are common to both the planes.

Solution. Intercepts of the plane (101) with the axes

$$= 1/1, \; 1/0 \text{ and } 1/1$$

$$= 1, \; \infty \text{ and } 1$$

Intercepts of the plane (111) with the axes $= 1, 1 \text{ and } 1$

Taking the point O as origin and the lines OA, OB and OC as the
axes **a**, **b** and **c** respectively, the plane with
intercepts 1, ∞ and 1 is the plane ADGC and that
with intercepts 1, 1 and 1 is plane ABC as shown
in Fig. 1.27. Therefore, the line common to both
the planes is the line AC. It corresponds to two
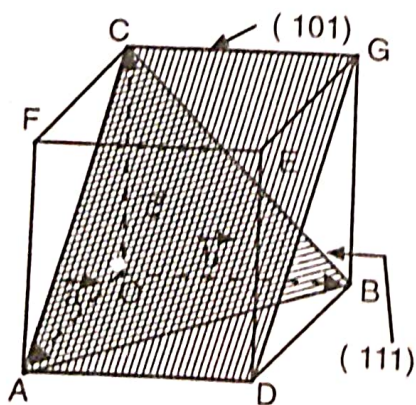directions, i.e., AC and CA.

Fig. 1.27. *Planes (101) and
(111) in a cubic lattice.*

Projections of the direction AC on the
axes = –1, 0 and 1

Projections of the direction CA on the
axes = 1, 0 and –1

Therefore, the required indices are $[\bar{1}01]$ and $[10\bar{1}]$.

Example 1.3. A plane makes intercepts of 1, 2 and 0.5Å on the crystallographic axes of an orthorhombic crystal with $a:b:c = 3:2:1$. Determine the Miller indices of this plane.

Solution. Taking the lengths of the axes OA, OB and OC as 3, 2 and 1Å respectively, the plane with intercepts of 1, 2 and 0.5Å on the axes is the plane DBE as shown in Fig. 1.28. The intercepts of this plane relative to full lengths of the axes are
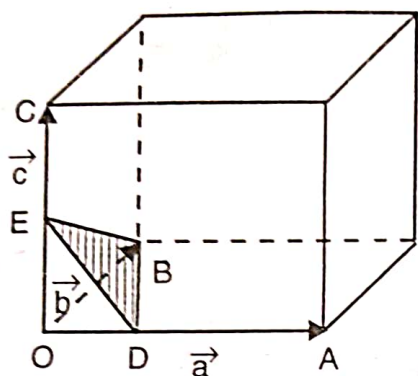

Fig. 1.28. *Plane (312) in an orthorhombic lattice.*

1/3, 2/2 and 0.5/1

or   1/3, 1 and 1/2

Reciprocals : 3, 1 and 2

Therefore, the Miller indices of the plane DBE are (312).

Example 1.4. In a cubic unit cell, find the angle between normals to the planes (111) and (121).

Solution. Since the crystal is cubic, the normals to the planes (111) and (121) are the directions [111] and [121] respectively. Let θ be the angle between the normals.

$$\therefore \quad \cos\theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{(h_1^2 + k_1^2 + l_1^2)^{1/2}\ (h_2^2 + k_2^2 + l_2^2)^{1/2}}$$

$$= \frac{1\times1+1\times2+1\times1}{(1^2+1^2+1^2)^{1/2}\ (1^2+2^2+1^2)^{1/2}}$$

$$= 0.9428$$

or $\theta = 19.47°$ or $19°28'$

Example 1.5. Calculate the packing efficiency and density of sodium chloride from the following data :

Radius of sodium ion $= 0.98$ Å

Radius of chloride ion $= 1.81$ Å

Atomic mass of sodium $= 22.99$ amu

Atomic mass of chlorine $= 35.45$ amu

Solution. The unit cell of NaCl strucutre is shown in Fig. 1.25. The Na^+ and Cl^- ions touch along the cube edges.

$\therefore$ Lattice parameter, a $= 2$ (Radius of Na^+ + Radius of Cl^-)
                    $= 2 (0.98 + 1.81) = 5.58$ Å

$$\text{Packing fraction} = \frac{\text{Volume of ions present in the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{4(4/3)\pi r_{N_a^+}^3 + 4(4/3)\pi r_{Cl^-}^3}{a^3}$$

$$= \frac{16\pi}{3}\left[\frac{(0.98)^3 + (1.81)^3}{(5.58)^3}\right]$$

$$= 0.663 \text{ or } 66.3\%$$

$$\text{Density} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{4(22.99 + 35.45) \times 1.66 \times 10^{-27}}{\left(5.58 \times 10^{-10}\right)^3} \text{ kg m}^{-3}$$

$$= 2234 \text{ kg m}^{-3} \text{ or } 2.23 \text{ g cm}^{-3}$$

SUMMARY

1. The solids may be broadly classified as crystalline and non-crystalline (or amorphous). The crystalline solids may be further sub-divided into single crystals and polycrystalline materials.

2. Crystallography is the study of formation, structure and properties of crystals.

3. A crystal structure results from the combination of a space lattice and a basis. A space lattice is a regular arrangement of infinite number of imaginary points in three-dimensional space. A basis is a structural unit comprising a single atom or a group of atoms which is placed on each lattice point in a regular fashion to generate the crystal structure.

4. A unit cell is a small group of points which acts as a building block for the entire lattice. It may be primitive or non-primitive. A primitive cell is the smallest volume unit cell and contains only one lattice point per cell. A non-primitive cell contains more than one lattice points per cell. The conventional unit cell has the highest possible symmetry and the lowest possible volume. It may be primitive or non-primitive.

5. The effective number of lattice points belonging to a unit cell is

$$N = N_i + N_f/2 + N_c/8$$

where N_i, N_f and N_c denote the number of lattice points present inside, at the face centres, and at the corners of the cell respectively.

6. A crystal remains invariant under the application of various symmetry operations like translation, rotation, reflection, inversion etc. Some rotational operations, such as 5-fold and 7-fold rotations, are not permissible as these are not compatible with lattice translation symmetry.

7. A point group is the combination of certain symmetry operations like rotation, reflection and inversion. It determines the symmetry of space around a point. The number of point groups in three-dimensional space is 32. These point groups produce only 14 Bravais lattices.

8. The set of all the symmetry elements of a crystal structure is called the space group. The number of distinct space groups possible in three dimensions is 230.

9. The Miller indices of a crystallographic plane and a direction are denoted by (hkl) and $[hkl]$ respectively where h, k and l are integers. The parallel planes and the parallel directions have the same indices.

10. The angle between two directions $[hkl]$ and $[h'k'l']$ is given by

$$\cos\theta = \frac{hh' + kk' + ll'}{(h^2 + k^2 + l^2)^{1/2}(h'^2 + k'^2 + l'^2)^{1/2}}$$

11. The interplanar distance for the parallel (hkl) planes for an orthorhombic lattice is

$$d = (h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2}$$

where a, b and c are the lengths of the axes.

12. A close-packed structure is that in which each atom has twelve identical nearest neighbours. A close-packed structure may be either *fcc* or *hcp* with the following sequence of layers :

$$hcp : ......ABABABAB......$$
$$fcc : ......ABCABCABC......$$

VERY SHORT QUESTIONS

1. Define a single crystal.
2. How does a crystal differ from a grain?
3. What is short-range order?
4. What are amorphous materials? Give an example of such a material.
5. What is crystallography?
6. What is a unit cell?
7. How does a crystal differ from a lattice?
8. What is the maximum number of possible Bravais lattices?
9. What are Miller indices? What is their importance?
10. Write the indices of all the twelve edges of a cube.
11. Write the indices of all the face diagonals of a cube.
12. What is packing efficiency? What are its values for sc, *bcc*, *fcc* and *hcp* structures?
13. Give at least one example each of materials exhibiting *sc*, *bcc*, *fcc* and *hcp* structures.
14. Calculate the number of carbon atoms per unit cell of diamond.

SHORT QUESTIONS

1. Define primitive and non-primitive translation vectors. Which type of translation vectors are preferred for describing a lattice?
2. Prove that the crystals cannot have five-fold symmetry.
3. Differentiate primitive cell, non-primitive cell and conventional cell from one another. How is a Weigner-Seitz cell constructed?
4. Describe the scheme to determine the Miller indices of a plane. Show that the parallel planes have the same Miller indices.
5. What is the relationship between the Miller indices and reciprocal lattice vectors corresponding to any plane?
6. Find the Miller indices of cube faces and diagonal planes of a unit cube.

7. Explain the concepts of lattice, basis and crystal structure. How are they related ?

8. Draw primitive cells corresponding to *bcc* and *fcc* unit cells.

9. How does *hcp* structure differ from *bcc* structure?

10. What is Bravais lattice? What is the maximum number of Bravais lattices possible? How will you account for the existence of thousands of structures from these lattices?

11. The end-centred orthorhombic is one of the Bravais lattices but the end-centred tetragonal is not. Give reasons.

12. The primitive cell of *fcc* lattice is rhombohedral. Why then is the rhombohedral lattice included separately in the Bravais list?

13. State the points of similarity and difference of the monoatomic, *sc*, monoatomic *bcc*, and CsCl structures?

14. Calculate the volume of the primitive cell and the number of nearest neighbours for an *fcc* lattice.

15. Obtain an expression for the packing fraction for *hcp* structure.

16. Show that the *c/a* ratio for an ideal *hcp* lattice is $\sqrt{8/3}$.

17. Determine the values of packing fraction for *fcc*, *bcc* and *sc* structures.

18. Assuming one of the basis atoms lying at the origin, find the coordinates of the other atoms for an *hcp* structure.

19. Explain, without calculation, why *fcc* and *hcp* structures have the same packing factor.

20. Show that for a cubic lattice, the lattice constant, *a*, is given by

$$a = \sqrt[3]{\frac{n\,M}{N\,\rho}}$$

where the symbols have their usual meanings.

21. What type of lattice and basis do the following structures have :

    (i) Sodium chloride (ii) Diamond cubic ?

22. Diamond is the hardest substance known in spite of the fact that the packing fraction and the coordination number of carbon atom in the *dc* structure are quite low. Explain.

23. There are four vacant tetrahedral sites in a unit cell of the *dc* structure. Can four additional carbon atoms occupy these sites? Give reasons.

24. How many crystal directions constitute the family of body diagonals of a unit cube ? Draw all such directions.

LONG QUESTIONS

1. What are symmetry operations? Describe the principal symmetry operations applicable to a three-dimensional lattice. Show that the five-fold rotational axis is not permissible in case of lattices.

2. What are point group and space group? Give their number for two-and three-dimensional lattices. List all the point groups of a two-dimensional lattice.

3. Determine the interplanar spacing between the two parallel planes with Miller indices (h, k, l) in a cubic crystal of side a.

4. Which is the most densely packed structure amongst the various cubic structures? Determine the packing fraction and porosity of this structure. Can the porosity be reduced by some means? What type of solids generally exhibit this type of structure and why?

5. Draw a plan view of sodium chloride structure. In how many ways can this structure be interpreted?

6. Draw a plan view of *hcp* unit cell and give coordinates of all the atoms. Are all the atoms located at equivalent sites? Discuss implications of your answer.

7. Draw the following:

   (i) $[1\bar{1}1], [1\bar{2}1]$ and $[0\bar{1}2]$ directions in cubic and tetragonal lattices.

   (ii) $(\bar{1}11), (\bar{1}\bar{1}2)$ and $(2\bar{1}0)$ planes in cubic and orthorhombic lattices.

PROBLEMS

1. Find the Miller indices for planes with each of the following sets of intercepts:

   (i) $3a, 3b, 2c$;   (ii) $a, 2b, \infty$;   (iii) $5a, -6b, c$;
   (iv) $a, b/2, c$;   (vi) $a, b, -c$;   (vi) $a/2, b, \infty$

   where a, b and c are lattice parameters.

   $$((223), (210), (6\bar{5}\,30), (121), (111), (210))$$

2. Draw a $(1\bar{1}0)$ plane in a cubic unit cell. Show all the $<111>$ directions that lie on this plane and give the Miller indices of each direction.

   $$\left([111], [11\bar{1}], [\bar{1}\bar{1}1] \text{ and } [\bar{1}\bar{1}\bar{1}]\right)$$

4. A plane makes intercepts of 1, 2 and 3 Å on the crystallographic axes of an orthorhombic crystal with $a : b : c = 3 : 2 : 1$. Determine the Miller indices of this plane.

(931)

5. Determine the number of the nearest neighbours and the closest distance of approach in terms of lattice parameter for monoatomic *sc*, *bcc* and *fcc* structures.

(6, *a*; 8, $a\sqrt{3}/2$; 12, $a/\sqrt{2}$)

6. Calculate the linear density (number of atoms per unit length) along cube edge, face diagonal and body diagonal of an *fcc* unit cell of side length *a*.

[$1/a$, $\sqrt{2}/a$, $1/(a\sqrt{3})$]

7. Nickel (*fcc*) has the lattice parameter of 3.52 Å. Calculate the atomic planar density (number of atoms per unit area) on (100), (110) and (111) planes. Is it possible to pack the atoms more closely than in (111) plane ?

(1.61×10^{19}, 1.14×10^{19}, 1.86×10^{19} atoms m^{-2}; No)

8. Calculate the angles which [111] direction of a cubic lattice makes with [100] and [110] directions.

(54°44', 35°15')

9. Show (111) and (222) planes in a cubic unit cell of side *a*. Compute the distances of these planes from a parallel plane passing through the origin.

[$a/\sqrt{3}$, $a/(2\sqrt{3})$]

10. Calculate the distances between the adjacent parallel planes of the type (100), (110) and (111) in an *fcc* lattice of lattice constant *a*. Check the validity of the statement "The most close-packed planes are the most widely spaced."

[$a/2$, $a/(2\sqrt{2})$ and $a/(\sqrt{3})$]

11. Copper (*fcc*) has density of 8960 kg m^{-3}. Calculate the unit cell dimension and the radius of Cu atom, given the atomic mass of Cu as 63.54 amu.

(3.61 Å, 1.28 Å)

12. Prove that *c/a* ratio for an ideal *hcp* structure is 1.633.

13. Zinc (*hcp*) has lattice parameters *a* and *c* as 2.66 Å and 4.95 Å respectively. Calculate the packing fraction and density of zinc, given the atomic radius and the atomic mass of Zn as 1.31 Å and 65.37 amu respectively.

(62%, 7155 kg m^{-3})

14. Calculate the distance between two atoms of a basis of the diamond structure, if the lattice constant of the structure is 5 Å.

(2.17 Å)